X-ray photoelectron spectroscopic characterization of ultra-thin silicon oxide films on a Mo(100) surface

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Ultra-thin films of silicon oxides supported on a Mo(100) surface have been studied using X-ray photoelectron spectroscopy (XPS). The films were synthesized by evaporating Si onto the Mo surface in oxygen ambient and were subsequently characterized using XPS with respect to the chemical states of silicon and the composition of the film. It has been found that the silicon oxide, prepared at room temperature with a silicon deposition rate of \( \sim 1.2 \, \text{Å/min} \) and an oxygen pressure of \( 2 \times 10^{-5} \, \text{Torr} \), consisted of predominantly silicon dioxide with a small fraction of suboxides. Annealing to \( \sim 1300 \, \text{K} \) yielded a stoichiometric film of SiO\(_2\). The suboxides are believed to further react with oxygen forming SiO\(_2\) at an elevated temperature.

1. Introduction

Over the last decades, there have been numerous publications that have dealt with studies of silicon oxide thin films using surface science spectroscopies [1–18]. These previous studies have focused exclusively on the oxidation of silicon single crystal surfaces, addressing important issues such as the mechanism and kinetics of the thin film growth, structural and electronic properties of silicon dioxide, and the formation of silicon suboxides. These investigations have been mainly stimulated by important applications of silicon oxides in the fabrication of electronic devices, for example, metal/oxide/semiconductor transistors and SiO\(_2\)/Si solar energy cells.

Silicon dioxide is also extensively used as a catalyst support in the chemical industry. However, the surface chemistry of bulk silica has been studied far less with surface science spectroscopies compared to SiO\(_2\)/Si interfaces. This is mainly because of the highly insulating and brittle properties of silica which often cause experimen-
tal difficulties such as surface charging, sample mounting, sample heating and cooling. In order to circumvent these difficulties and to exploit microscopic processes on a silica surface using surface analytical techniques, experiments have been recently conducted to synthesize and characterize ultra-thin films of silicon oxide on a refractory metal surface [19,20]. Furthermore, thin films of SiO\(_2\) prepared in this manner allow much greater flexibility with respect to thermal processing compared to SiO\(_2\) films on silicon in that films of SiO\(_2\) on molybdenum are stable up to 1500 K. Similar studies have been performed on other catalytically important oxides such as magnesium oxide [21] and iron oxides [22].

In previous studies of silicon oxide thin films on a Mo(110) surface using temperature programmed desorption (TPD), Auger electron spectroscopy (AES), electron energy loss spectroscopy (ELS) and infrared reflection absorption spectroscopy (IRAS) [19,20], it was found that a SiO\(_2\) film can be synthesized by evaporating silicon in a low background pressure of oxygen at a sample temperature of \( \sim 300 \, \text{K} \). The gas phase precursors for the SiO\(_2\) film were reported to be SiO
which was produced by oxidative etching of the Si source. The as-deposited films mainly consist of SiO\(_2\), as indicated by the AES spectra. The SiO\(_2\) film annealed to \( \sim 1400 \) K exhibited electronic and structural properties similar to those of vitreous silica. The thermal stability of the SiO\(_2\) film was found to depend on the film thickness. Annealing a thin SiO\(_2\) film (< 50 Å) to 1500 K caused a reduction of the film by the Mo substrate, forming the volatile products SiO and MoO\(_3\).

Recently, we have further examined the silicon oxide thin films grown on a Mo(100) surface with X-ray photoelectron spectroscopy (XPS), addressing the effects that oxygen ambient pressure and annealing temperature have on the chemical states of Si and the composition of the films. The results are presented and discussed in this paper.

2. Experimental

The experiments were carried out in an ultrahigh vacuum chamber equipped with XPS, TPD and low energy electron diffraction (LEED). A detailed description of this chamber has been given elsewhere [23].

The Mo(100) crystal was spot-welded onto a 0.2 mm Ta wire that allowed cooling of the crystal to 90 K and resistive heating to 1400 K. In addition, the sample could be heated to 2300 K using e-beam heating. A W-5%Re/W-26%Re thermocouple was spot-welded onto the sample’s back face for temperature measurement. The Mo(100) surface was cleaned using the procedure described in ref. [24].

The silicon source used for deposition was a high purity Si block (~ 1 x 1 x 3 mm\(^3\)) wrapped by a tantalum heating wire. The Si source was degassed extensively prior to each dosage. The Si oxide films, synthesized in this work, showed no C, S or N impurities within the XPS and AES detection limit (< 1 at%). The thickness of the films was estimated using the electron mean free path (23 Å) in SiO\(_2\) films for Mo(3d) photoelectrons, which have a kinetic energy of 1020 eV with the Mg K\(\alpha\) X-ray source (1253.6 eV) [25,26].

The Si oxide deposition rate varies with both oxygen pressure and the Si source temperature, and was controlled at approximately either 0.6 or 1.2 Å/min for this work.

In the present study of the SiO\(_2\)/Mo(100) surfaces, the core level binding energies were measured with reference to the Mo(3d\(_{5/2}\)) binding energy at 277.7 eV [27]. The pass energy of the spectrometer was 40 eV for this work, and the substrate Mo(3d\(_{5/2}\)) peak exhibited a full width at half maximum (FWHM) of 1.4 eV which can be taken as the instrumental resolution. The XPS spectra in this paper were acquired using Mg K\(\alpha\) X-rays (1253.6 eV).

3. Results

Fig. 1 shows the Si(2p) XPS spectra for silicon oxide thin films that were prepared at three different oxygen background pressures. The thicknesses of the films are estimated to be 36 Å. At an oxygen ambient pressure of \( 1 \times 10^{-8} \) Torr, spectrum a exhibits a significant peak at 99.4 eV that corresponds to silicon. This value is 0.2 eV higher than the Si(2p) binding energy (99.2 eV) from a pure silicon crystal [27]. The peak at \( \sim 102.5 \) eV is broad, and is thus best decomposed into two peaks using mixed Gaussian-Lorentzian curve fitting. These two peaks at 103.2 and 101.7 eV correspond to oxidized silicon. As the oxygen pressure increases (spectra b and c), the 103.2 eV peak intensity increases along with a shift in its peak position to higher binding energy, the intensity of the 101.7 eV peak first increases and then decreases, and the intensity of the peak at 99.4 eV decreases considerably. In spectrum c, the 103.6 eV peak shows a binding energy similar to that for silicon dioxide (103.4 eV), and the peak at 102.7 eV falls in the binding energy range of suboxides (SiO\(_x\), with \( x < 2 \)) [2–8,27]. Therefore, we assign these two peaks at 103.6 and 102.7 eV to correspond to SiO\(_2\) and suboxides, respectively. Previous studies also indicated that the oxide films prepared at an oxygen pressure of \( 1 \times 10^{-5} \) Torr with a deposition rate of \( \sim 1 \) Å/min consist predominantly of silicon dioxide, as evidenced by AES and FIES spectra [19,20].
Fig. 1. The Si(2p) XPS spectra of silicon oxide films (36 Å) on a Mo(100) surface. The films were prepared by evaporating Si in an O₂ pressure of 1×10⁻⁸ Torr (a), 5×10⁻⁸ Torr (b) and 2×10⁻⁵ Torr (c). The substrate temperature during the film preparation was ~350 K. The oxide deposition rate was approximately 1.2 Å/min.

Fig. 2. The Si(2p) XPS spectra of silicon oxide films (36 Å) on a Mo(100) surface. The films were prepared by evaporating Si in an O₂ pressure of 2×10⁻⁵ Torr with a dosing rate of ~1.2 Å/min. The substrate temperature during the film preparation was ~350 K. The film was then annealed to 393 K (a), 1023 K (b) and 1373 K (c).
Fig. 3. The Si(2p) XPS spectra of silicon oxide films (36 Å) on a Mo(100) surface. The films were prepared by evaporating Si in an O₂ pressure of 5 × 10⁻⁷ Torr with a dosing rate of ~1.2 Å/min. The substrate temperature during the film preparation was ~350 K. The film was then annealed to 373 K (a), 803 K (b) and 1198 K (c).

Significant increase in the Si peak area. Further annealing to 1373 K eliminates the silicon peak with a highly symmetric peak of SiO₂ remaining.

Fig. 3a is the XPS spectrum for a silicon oxide film that was dosed at relatively low O₂ pressure (5 × 10⁻⁷ Torr). This film consists of 26% SiO₂, 38% SiOₓ, and 36% Si, as estimated from the areas of the deconvoluted peaks. Annealing to 803 K causes a significant increase in the SiO₂ peak intensity with a concurrent decrease in the intensities of SiOₓ and of Si. Spectrum c, collected after annealing the film to 1198 K, exhibits virtually no suboxide peak, and the Si peak intensity has been significantly decreased when compared to that of spectrum a. Fig. 3 demonstrates that the film synthesized at relatively low oxygen pressure has a considerable amount of suboxides and Si. This is consistent with previous studies, which showed that the film prepared at an oxygen pressure less than 1 × 10⁻⁶ Torr contained silicon or silicon suboxides [19,20]. Annealing the film to elevated temperatures was found to remove the suboxide spectral features [19]. We will discuss this SiOₓ in more detail in the following section.

The O(1s) spectra for a silicon oxide film are shown in fig. 4. After the film preparation at 310 K, the O(1s) spectrum indicates a single peak with a binding energy of 533.0 eV. This peak exhibits a symmetric lineshape with a full width at half maximum (FWHM) of 2 eV, identical to that reported for a thick SiO₂ film grown on a silicon surface [18]. Annealing this film to 1373 K causes a 0.3 eV shift in the peak maximum with no noticeable change in the peak width or peak shape.

Fig. 4. The O(1s) XPS spectra of a silicon oxide film (100 Å). The film was prepared by evaporating Si at an oxygen pressure of 1 × 10⁻⁵ Torr with a dosing rate of ~0.6 Å/min at a sample temperature of 300 K. The film was then annealed to the indicated temperatures.
Fig. 5 shows the plots of the Si(2p) and O(1s) binding energies and the ratio of the integrated intensity of O to Si as a function of annealing temperature. The silicon oxide film was synthesized in an oxygen pressure of $1 \times 10^{-5}$ Torr with a dosing rate of $0.6$ Å/min at room temperature. Upon annealing to 800–1300 K, the O(1s) binding energy shifts 0.3 eV and the Si(2p) shifts 0.4 eV toward a higher binding energy. The integrated intensity ratio of O to Si shows an increase in the 1100–1350 K annealing temperature range. Since all the experimental evidence, including the XPS spectra in fig. 2 and the TPD, AES and ELS spectra in previous work [19,20], have indicated that both suboxides and Si have been totally eliminated from the film at an annealing temperature of $\sim 1300$ K, we assign the ratio corresponding to the spectra at 1480 K to be two, the atomic ratio of O to Si in SiO$_2$. In the calculation of the ratios, the contribution of oxygen from the Mo substrate has been subtracted. The O(1s) binding energies are 533.0 eV for SiO$_2$ and 530.7 eV for O chemisorbed on Mo(100), and thus are easily discernable at a low coverage of SiO$_2$.

Finally, we present the Mo(3d) XPS spectra for a SiO$_2$/Mo(100) surface at several annealing temperatures. The Mo(3d$_{5/2}$) peak has a FWHM of 1.3 eV and a binding energy of 227.7 eV for all the spectra. These values remain unchanged in the 1023–1473 K annealing temperature range. Deposition of SiO$_2$ and subsequent annealing cause no measurable change in the Mo substrate. The intensity increase in the 1473 K spectrum is due to the desorption of SiO$_2$ [20].

4. Discussion

One of the primary goals of synthesizing silicon oxide on a Mo surface is to prepare a stoichiometric silica film that can be used for model catalyst studies. Figs. 1–3 indicate that such a silica film can be obtained by evaporation of Si with an oxygen pressure of $2 \times 10^{-5}$ Torr at a deposition rate of $\sim 1.2$ Å/min, followed by annealing the film to 1300 K. At a relatively low oxygen pressure ($< 5 \times 10^{-8}$ Torr), the film has a significant amount of suboxides and silicon in coexistence with SiO$_2$. Fig. 1 further indicates that the film synthesized at room temperature contains more than 10% of suboxides even with an oxygen pressure of $2 \times 10^{-5}$ Torr at a deposition rate of $\sim 1.2$ Å/min, followed by annealing the film to 1300 K. A further increase in oxygen pressure produces little improvement in the film composition. Annealing to 1300 K, however, eliminates the suboxides and silicon and results in a film consisting of only SiO$_2$. The silica film has been suggested to assume a vitreous SiO$_2$ structure in which the basic $[\text{SiO}_4]$ blocks are networked via bridging oxygen atoms [19,20]. This film showed no LEED pattern and thus lacks long range order.

The suboxide species formed during oxidation of silicon surfaces have been extensively studied
with a variety of spectroscopies including XPS [2-9], ELS [3,10-12] and IRAS [13-15]. It is generally believed that the SiO\textsubscript{x} species are located at the SiO\textsubscript{2}/Si interface with a thickness of a few ångströms. In studies of oxygen adsorption on Si surfaces, suboxide species were also observed for a monolayer surface oxide [8,11]. An investigation of silicon oxidation by means of ion implantation at room temperature has indicated the formation of a thin layer inside a Si crystal which contains a mixture of SiO\textsubscript{2}, SiO\textsubscript{x} and Si [4]. The SiO\textsubscript{x} species, investigated by both high resolution XPS spectra [7,8] and theoretical calculations [5], consist of all four of the Si oxidative states, Si\textsuperscript{4+}, Si\textsuperscript{2+}, Si\textsuperscript{3+} and Si\textsuperscript{1+} with the Si(2p) core level shifts of 0.6, 1.5, 2.8 and 4.5 eV, respectively. Therefore, we believe that the suboxide film prepared at room temperature in this work may contain all four oxidative states. The shift in the maxima of the oxide peaks towards a higher binding energy (fig. 1), as the oxygen pressure increases, reflects the increase in the relative population of the higher oxidative states. At an annealing temperature of 1300 K, the film is present as pure SiO\textsubscript{2}. The peak in fig. 2c indicates a chemical shift of 4.4 eV relative to the binding energy of Si (99.2 eV). This value is in good agreement with those (4.3-4.5 eV) of SiO\textsubscript{2} reported in previous publications [4,7,8,27].

The XPS peaks corresponding to silicon in figs. 1-3 exhibit binding energies of 99.4-99.9 eV, a few tenths of an eV higher than that of single crystal Si (99.2 eV) [27]. This difference may be due to the fact that the silicon atoms are intermixed with the silicon oxides and thus are electronically perturbed with respect to bulk Si. It is also possible that the Si peaks are a convolution of Si and Si\textsuperscript{1+}. This would also shift the maximum of the resultant peak to a higher binding energy.

The binding energy and symmetric lineshape of spectrum c in fig. 2 indicate that the film consists of only SiO\textsubscript{2}. The stoichiometry was calculated using the integrated intensities of Si and O, normalized by the atomic sensitivity factors [27]. This calculation yielded an O to Si atomic ratio of 2:1, further confirming the existence of a single phase of SiO\textsubscript{2} in the film. The stoichiometry of the film prepared at room temperature without annealing is estimated to be 1.7:1, consistent with a film which has a composition of 82% SiO\textsubscript{2}, 13% suboxide and 5% silicon as shown in the fig. 2a.

The disappearance of the SiO\textsubscript{x} species from the film upon annealing is likely via reaction with oxygen within the film to form SiO\textsubscript{2}. This reaction is apparent by the increase in the SiO\textsubscript{2} peak intensity and a concurrent decrease in the SiO\textsubscript{x} peak intensity (figs. 2 and 3), while the stoichiometry of the film remains unchanged in the 400-1000 K annealing temperature range (fig. 5). The interaction between SiO\textsubscript{x} and O upon annealing has also been observed in previous studies of the oxidation of Si crystals [4,6]. The oxygen involved in the post reaction in the present work was likely trapped in the film during SiO\textsubscript{2} synthesis [5] or was contributed by the decomposition of [SiO\textsubscript{x}] moieties [19,20]. The increase in the film stoichiometry at 1100-1400 K is associated with the disappearance of the Si peak in fig. 2. The Si appears to have interacted with SiO\textsubscript{2} to form volatile SiO that immediately desorbed [20].

The O(1s) spectra of the silicon oxide film show a single peak with a binding energy of 533.0 eV and a FWHM of 2 eV, both identical to the values reported for bulk SiO\textsubscript{2} [18]. It seems that the oxygen involved in the SiO\textsubscript{x} post-oxidation has a binding energy similar to that of O in SiO\textsubscript{2} and thus is not discernable in the present XPS spectra. Annealing the film to 1373 K causes a 0.3 eV shift toward a higher binding energy (figs. 4 and 5). The Si(2p) peak also shifts 0.4 eV upwards (fig. 5). The variation of O(1s) and Si(2p) binding energies has been measured in detail as a function of the thickness of the SiO\textsubscript{2} films on Si [18]. The present study also found that the Si(2p) and O(1s) binding energies change with the film thickness. These shifts can be attributed to several physical processes such as extra-atomic relaxation due to a high defect concentration [18], band bending in the SiO\textsubscript{2} film that causes a static surface potential change [28,29], or a local charging effect as the small islands of SiO\textsubscript{2} nucleate into large clusters.

Fig. 6 shows that upon film deposition and subsequent annealing of the sample, the Mo(3d)
stoichiometric SiO$_2$ film can be obtained with a Si deposition rate of $\sim 1.2$ Å/min at an oxygen pressure of $2 \times 10^{-5}$ Torr at 300 K, followed by an annealing of the film to $\sim 1300$ K. The film prepared at room temperature without annealing was found to contain a small fraction of suboxides and silicon which undergo post-oxidation at an elevated temperature, forming either SiO$_2$ or volatile SiO.

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References